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(54) Title: REPLACEMENT REFRIGERANT COMPOSITION

(57) Abstract

A refrigerant composition for use in a vapour-compression refrigeration apparatus as a replacement for currently used refrigerants R22 and R12 comprises a mixture of pentafluoroethane (R125), tetrafluoroethane (R134a), a hydrocarbon selected from isobutane (R600a) and propane (R290), and optionally octafluoroethane (R218). The composition contains no chlorine atoms and is non-depleting to atmospheric ozone; but specific compositions have pressure-temperature relations substantially the same as R22 and R12 thereby allowing their use as direct replacements therefor in existing refrigeration apparatus.

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REPLACEMENT REFRIGERANT COMPOSITION

TECHNICAL FIELD

The present invention relates to a refrigerant composition, which contains no chlorine atoms.

BACKGROUND

Chlorofluorocarbon (CFC) gases, such as refrigerant R12 (CCl_2F_2), have been used for many years as refrigerants and are especially used in domestic refrigerators and car air conditioning systems. However, such gases have been implicated in environmental damage. These gases, which are very inert, are released from refrigeration systems at ground level and diffuse into the upper atmosphere. Because of their inertness, the gases are able to survive without decomposition until they reach the stratosphere where they are broken down by ultra-violet radiation, releasing chlorine atoms which catalyse breakdown of the stratospheric ozone layer. There has recently been considerable concern about reduction in stratospheric ozone levels and this has led to proposed restrictions and prohibitions on certain CFC's.

Other refrigerants such as chlorodifluoromethane (R22) are environmentally less objectionable as they tend to be degraded naturally at lower levels of the atmosphere before reaching the ozone layer. However, R22 contains

chlorine and is still considered to contribute to ozone depletion. Further, R22 has a higher index of compression than, for example, R12, such that compressor discharge temperatures become excessive at pressure ratios which would not cause excessive discharge temperatures if R12 were being used.

It is among the objects of the present invention to provide a refrigerant composition which does not contain any chlorine but which has acceptable refrigerant characteristics for use in vapour compression refrigerators as a replacement for refrigerant R22 and/or R12 in existing refrigeration equipment.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention there is provided a refrigerant composition for use in a refrigeration apparatus which comprises a mixture of:

(i) pentafluoroethane;

(ii) tetrafluoroethane; and

(iii) a hydrocarbon selected from isobutane, propane and mixtures thereof.

The composition may optionally also contain (iv) octafluoropropane.

A further aspect of the present invention provides a method of refrigeration which employs the composition as a refrigerant medium, particularly a vapour-compression refrigerator.

A still further aspect provides a refrigeration apparatus which employs the composition as a refrigerant medium, particularly a vapour-compression refrigerator.

None of the components of the mixture contribute to ozone depletion nor are any toxic to humans. Further, the mixture may be used with a variety of existing lubricants as conventionally used in vapour compression refrigeration apparatus, including mineral oil lubricants, alkylbenzene lubricants and polyolester lubricants. Specialised lubricants are not required.

It is found that by forming mixtures of these three or four components in chosen proportions, it is possible to provide refrigerant compositions which have pressure-temperature relationships which are sufficiently similar to those of the current refrigerants R22 and R12 to allow their use as replacements therefor in existing refrigeration equipment. The pressure-temperature relationship refers to the vapour pressure of the refrigerant composition at various temperatures corresponding to those used in the refrigeration apparatus. Thus, the design pressure capabilities of the apparatus are not exceeded. It is also found that the refrigeration capacities of the compositions of the invention may be arranged to be similar to those of the current refrigerants R22 and R12, so that the refrigeration capacity (i.e. the amount of cooling produced) of refrigeration apparatus intended to be used

with R22 or R12 respectively is substantially unaffected.

Advantageously, the compositions of the invention tend to have lower compressor discharge temperatures than the corresponding conventional refrigerant.

The pentafluoroethane (R125) is preferably present in an amount of 0.5 to 60 wt%, particularly 1 to 50 wt %. In compositions for use as an R22 replacement, R125 is preferably present in percentages at the upper end of this range e.g. 20 to 45 wt %, particularly 27 to 40 wt %. In compositions for use as an R12 replacement, the amount of R125 is usually at the low end of this range e.g. 0.5 to 10 wt%, especially 1 to 10 wt.%.

The tetrafluoroethane (preferably R134a) is generally present in an amount of 30 to 98 wt%, particularly 30 to 90 wt.%, and usually forms the major proportion of the composition. When used as an R22 replacement, the composition of the invention usually employs 45 to 70% of R134a; whereas for use in replacing R12 the percentage of R134a usually lies in the range 80 to 90 wt.%.

For safety reasons, the hydrocarbon should preferably be present in a non-flammable proportion so that in the event of a leak of refrigerant medium into the atmosphere, no explosive or flammable mixture is produced. A hydrocarbon content of 1 to 11 wt%, particularly 2 to 10 wt.%, and preferably 3 to 5 wt.% is preferred. In particular, a non-flammable composition is one which contains the components of the mixture in such a ratio

that when the composition is mixed with air in practical proportions (e.g. in the event of a leak) no flammable mixture results. The fluorocarbon components R125 and R218 possess fire-retardant properties to a degree. Thus, the assessment of flammability characteristics is not necessarily predictable but can be determined by routine experimentation (see, for example, our patent US 5108637).

The octafluoropropane (R218) is an optional constituent and is typically present in an amount of 0 to 20 wt.%. It has a long lifetime when released into the atmosphere so that future legislation may make its use less preferred. It is generally present in an amount of 4 to 15 wt%, particularly 5 to 10 wt.%.

In a preferred embodiment as an R22 replacement, the composition comprises a mixture of:

(i) 20 to 45 wt% pentafluoroethane (R125);

(ii) 45 to 70 wt% tetrafluoroethane (e.g. R134a);

(iii) 2 to 8 wt% isobutane (R600a); and

(iv) 5 to 10 wt% octafluoroethane (R218).

The pressure-temperature relationship of this mixture is similar to that of chlorodifluorethane (R22). The refrigerating performance is also similar within acceptable limits. However, the mixture has a lower index of compression than R22, resulting in lower compressor discharge temperatures, and of course contains no chlorine.

A preferred embodiment for use as an R12 replacement comprises a mixture of:

(i) 0.5 to 5 wt% pentafluoroethane (R125);

(ii) 75 to 98 wt% tetrafluoroethane (R134a);

(iii) 1 to 6 wt% isobutane (R600a); and

(iv) 6 to 15 wt% octafluoroethane (R218).

DESCRIPTION OF PREFERRED EMBODIMENTS

These and other aspects of the present invention will now be described, by way of example in conjunction with the drawings; wherein.

Figure 1 shows the pressure-temperature diagrams for a composition according to the invention (RX3) and conventional R22 refrigerant; and

Figure 2 shows the pressure-temperature diagrams for a further composition according to the invention (RX2) and conventional R12 refrigerant.

The composition according to the invention (RX3) comprised 40 wt.% R125, 6 wt.% R218, 50 wt.% R134a and 4 wt.% R600a and is intended as a replacement for currently used R12 refrigerant.

The composition in liquid form was introduced into an evacuated vessel and allowed to equilibrate. The vessel was heated to various temperatures and the vapour pressure in the presence of liquid noted. It can be seen from Figure 1 that the pressure-temperature relationship is very similar to that for R22, which means that the pressures encountered using the composition of the invention will not in substance exceed those of R22. Thus

the design pressures of the apparatus will not be exceeded.

Figure 2 shows the pressure-temperature relationship for a further composition (RX2) according to the invention in comparison to conventional R12 refrigerant. This was obtained following the procedure described in relation to Figure 1.

The composition (RX2) according to the invention comprised 1 wt% R125, 9 wt% R218, 87 wt% R134a and 3 wt% R600a.

It will be noted that the pressure-temperature relationship for RX2 is very similar to R12, so that it is suitable as a chlorine-free replacement therefor without requiring substantial changes to the refrigeration apparatus.

EXAMPLE

A water chilling system in everyday use and employing refrigerant R12 developed a leak at the hermetically sealed motor terminals. The leak was repaired and the compressor replaced. The system was evacuated and recharged with refrigerant composition RX2 according to the invention of composition given above. Table 1 shows performance characteristics before and after charging with RX2.

The performance using RX2 according to the invention is similar or slightly better than the performance using conventional refrigerant R12.

In Table 1 the abbreviations have the following meanings.

SUCT PRESS and DISCH PRESS are the compressor suction and discharge pressures, respectively.

SUCT TEMP COMP and DISCH TEMP EVAP COIL are compressor suction and discharge temperatures, respectively.

SUCT TEMP EVAP COIL is the suction temperature at the evaporator coil.

LIQ TEMP BEFORE and AFTER HEAT EXCH are the respective temperatures before and after the heat exchanger.

TABLE 1

(WATER CHILLER - REFRIGERANT RX2 as replacement for R12)

R12	SUCT PRESS psig	DISCH PRESS psig	SUCT TEMP COMP °C	DISCH TEMP COMP °C	SUCT TEMP EVAP COIL °C	LIQ TEMP BEFORE HEAT EXCH. °C	LIQ TEMP AFTER HEAT EXCH. °C	WATER TANK TEMP °C
1	30	140	16	57.7	12.7	30.5	11.5	13.2
2	28	130	15.8	62.4	8.5	28.5	11.0	9
3	22	130	13	65	4.9	28	12.4	4.5
RX2	NEW COMPRESSER AND REFRIGERANT CHARGE							
1	20	140	14	69	4	38	33	3.5
2	20	150	14	74	6	38	36	3
3	20	145	13	70	4.5	37	36	2.5
4	20	143	13	69	4.6	37	35.5	2.7
5	30	155	16	70	10.1	35	28	8
6	20	143	13	69	4	36	30	3

CLAIMS

1. A refrigerant composition for use in a refrigeration apparatus which comprises a mixture of:

(i) pentafluoroethane;

(ii) tetrafluoroethane; and

(iii) a hydrocarbon selected from isobutane, propane and mixtures thereof.

2. A composition according to any preceding claim wherein the pentafluorethane is present in an amount of 0.5 to 60 wt%.

3. A composition according to claim 2 wherein the pentafluoroethane is present in an amount of 1 to 50 wt%.

4. A composition according to any preceding claim wherein the tetrafluorethane is present in an amount of 30 to 98 wt%.

5. A composition according to claim 4 wherein the tetrafluoroethane is present in an amount of 30 to 90 wt%.

6. A composition according to any preceding claim wherein the hydrocarbon is present in an amount of 1 to 11 wt%, and the composition is non-flammable.

7. A composition according to claim 6 wherein the hydrocarbon is present in an amount of 2 to 10 wt%.

8. A composition according to any preceding claim wherein the hydrocarbon is isobutane.

9. A composition according to any preceding claim which further comprises:

(iv) octafluoropropane.

10. A composition according to claim 9 which comprises up to 20 wt% of octafluoropropane.

11. A composition according to claim 10 wherein the octafluoropropane is present in an amount of 5 to 10 wt%.

12. A refrigerant composition for use as a replacement for refrigerant R22 in a refrigeration apparatus which comprises a mixture of:

(i) 20 to 45 wt% pentafluoroethane;
(ii) 45 to 70 wt% tetrafluoroethane;
(iii) 2 to 8 wt% isobutane; and
(iv) 5 to 10 wt% octafluoroethane.

13. A refrigerant composition fur use as a replacement for refrigerant R12 in a refrigeration apparatus which comprises a mixture of:

(i) 0.5 to 5 wt% pentafluoroethane;

(ii) 75 to 98 wt% tetrafluoroethane;

(iii) 1 to 6 wt% isobutane; and

(iv) 6 to 15 wt% octafluoroethane.

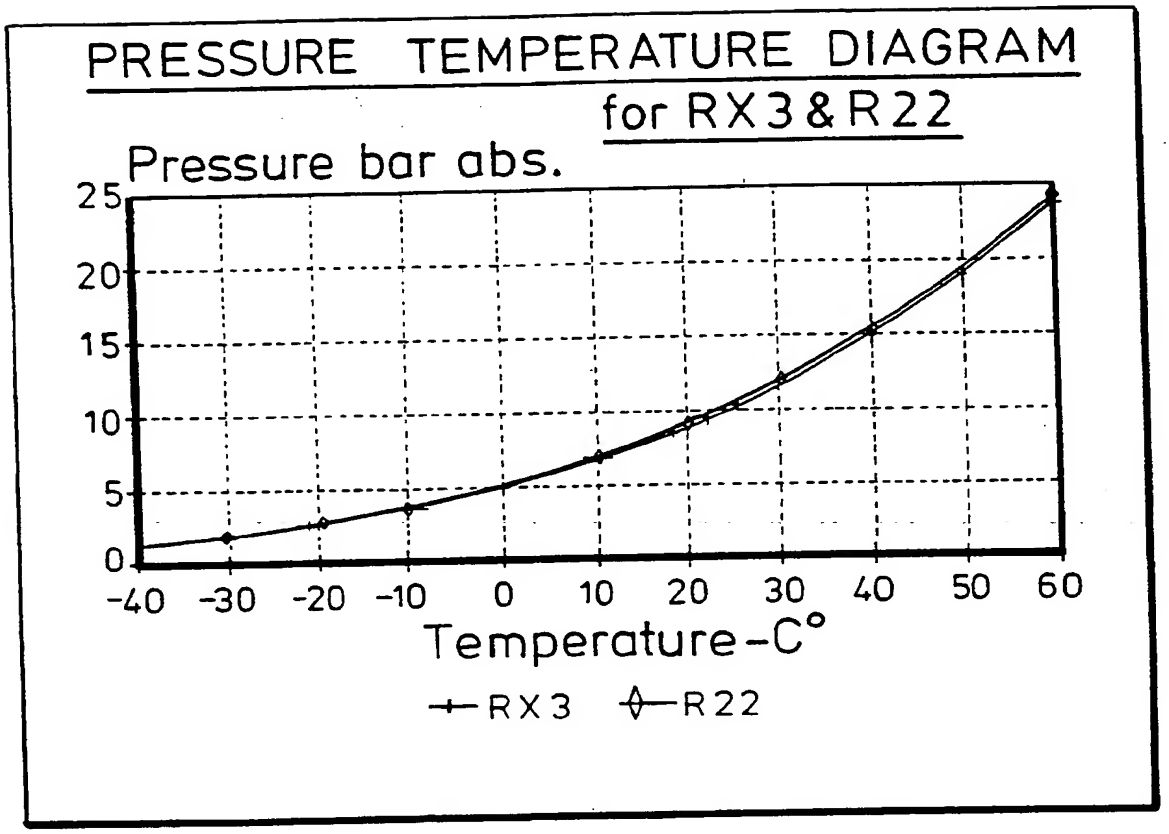

FIG. 1

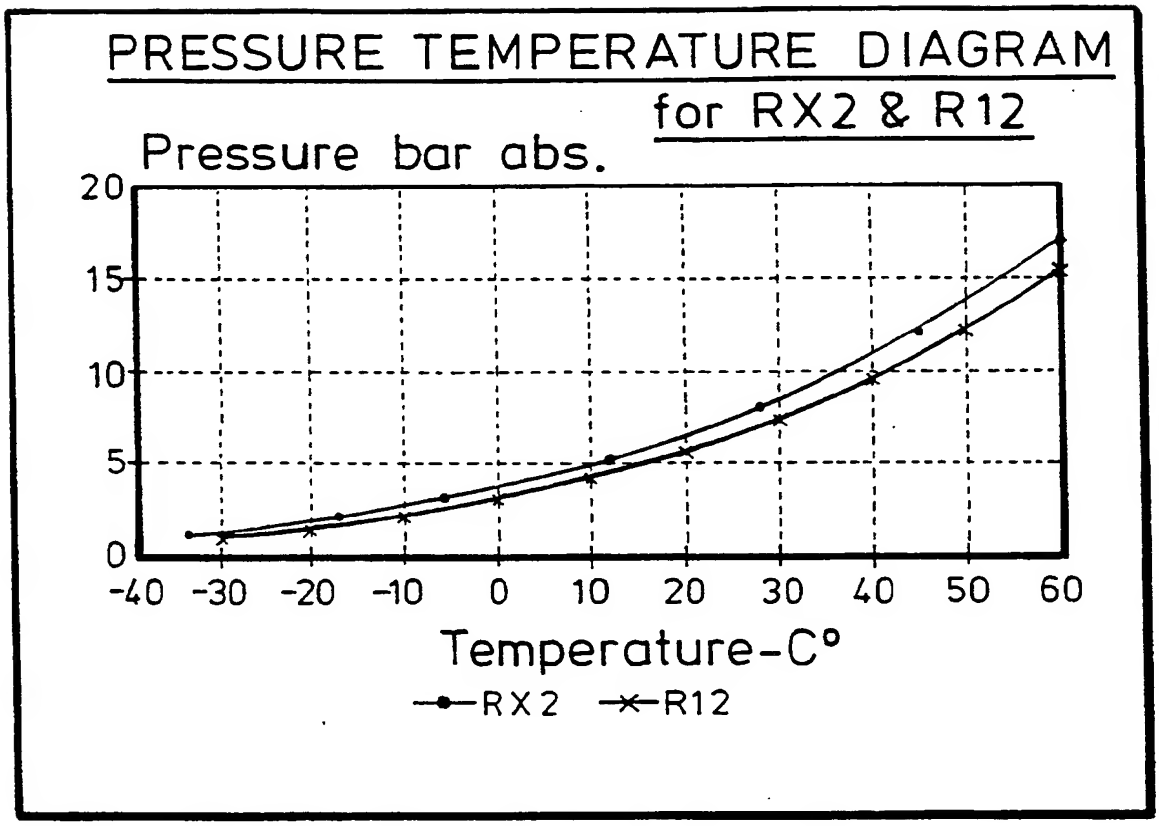

FIG. 2

INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/GB 94/02042

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 478 (C-1104) 31 August 1993 & JP,A,05 117 643 (MATSUSHITA ELECTRIC IND CO LTD) 14 May 1993 see abstract ---	1-7
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 176 (C-0934) 27 April 1992 & JP,A,04 018 485 (SANYO ELECTRIC CO LTD) 22 January 1992 see abstract ---	1-8
X	WO,A,93 15163 (ALLIED SIGNAL) 5 August 1993 see the whole document ---	1-7

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
6 December 1994	15. 12. 94

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Inter. application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 11338 (DU PONT DE NEMOURS) 9 July 1992 see abstract; claims 1,2,10,11	1-13
A	EP,A,0 539 952 (MATSUSHITA) 5 May 1993 see abstract; claims 1-6	1-13

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No
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